

Fe³⁺/ΣFe vs. FeLα peak energy for minerals and glasses: Recent advances with the electron microprobe

MICHEL FIALIN,^{1,*} CHRISTIANE WAGNER,² NICOLE MÉTRICH,³ ERIC HUMLER,⁴ LAURENCE GALOISY,⁵ AND ANTOINE BÉZOS⁴

¹Centre de Microanalyse Camparis-CNRS, Université Paris 6, 4 place Jussieu, 75252 Paris cedex 5, France

²Laboratoire de Pétrologie, Modélisation des Matériaux et Processus, Université Paris 6, 4 place Jussieu, 75252 Paris cedex 5, France

³Laboratoire Pierre Süe, UMR 9956-CNRS, CE-Saclay, 91191 Gif sur Yvette, France

⁴Laboratoire de Géosciences Marines-CNRS, Université Paris 6 et 7, Institut de Physique du Globe, 4 place Jussieu, 75252 Paris cedex 5, France

⁵Laboratoire de Minéralogie-Cristallographie, UMR 7590-CNRS, Universités Paris 6 et 7, Institut de Physique du Globe, 4 place Jussieu, 75252 Paris cedex 5, France

ABSTRACT

This paper describes a preliminary study that attempts to determine the oxidation state of Fe (Fe³⁺/ΣFe) with the electron microprobe (EMP) by measuring the self-absorption induced shift of the FeLα peak emitted from minerals and glasses. In transition metals of the first row, the L-spectra exhibit common distortions, namely peak position shifts, peak shape alterations, and changes in the Lβ/Lα ratios, caused by the large difference in the self-absorption coefficients (α/ρ) on either sides of the L₁ absorption edges that are in close proximity to the Lα peak maxima. Measurements performed on α-Fe₂O₃ and Fe₃O₄ oxides have shown that self-absorption effects are stronger for the later oxide, leading to enhanced Fe³⁺Lα peak shift toward longer wavelengths as the beam energy increases. First measurements performed on silicates have confirmed that enhanced self-absorption of FeLα occurs on Fe²⁺ sites. The measurements consisted of plotting the FeLα peak position at a fixed beam energy (15 keV) against the total Fe concentration for two series of Fe²⁺- and Fe³⁺-bearing silicates. In a first step, these data have shown that both Fe²⁺Lα and Fe³⁺Lα peaks shift continuously toward longer wavelengths as the Fe concentration increases, with enhanced shifts for Fe²⁺Lα. For silicates containing only Fe²⁺ or Fe³⁺, no effects of the site geometry were detected on the variations of the FeLα peak position. A second set of plots has shown the variations of the peak position relative to the previous Fe²⁺-Fe³⁺ curves of step 1, as a function of the nominal Fe³⁺/ΣFe, for a series of reference minerals (hydrated and non-hydrated) and basaltic glasses. Data from chain and sheet silicates (e.g., pyroxenes, amphiboles, micas) exhibited strong deviations compared to other phases (e.g., garnets, Al-rich spinels, glasses), due to reduced self-absorption of FeLα. Intervalence-charge transfer (IVCT) mechanisms between Fe²⁺ and Fe³⁺ sites may be the origin of these deviations. These crystal-structure effects limit the accuracy of the method for mixed Fe²⁺-Fe³⁺ valence silicates. Precisions achieved for further Fe³⁺/ΣFe measurements strongly depend on the total Fe concentration. For basaltic glasses containing an average of 8 wt% Fe and 10% Fe³⁺/ΣFe, the precision is about ±2% (absolute). For low Fe concentrations (below 3.5 wt%), the uncertainty in the peak position measured by the EMP spectrometers leads to error bars that are similar to with the separation of the curves fitted to the Fe²⁺ and Fe³⁺ plots, which is propagated as prohibitive lack of precision for Fe³⁺/ΣFe (>70% relative). A major limitation of microbeam methods in general deals with beam damage. This aspect has been carefully studied for basaltic glasses, and optimal beam conditions have been established (in general, electron doses higher than those corresponding to 130 nA and 30 μm beam diameter should be avoided to prevent large beam induced oxidation phenomena). Additional work, in progress, concerns: (1) other beam-sensitive phases such as hydrated glasses; and (2) minerals in which FeLα is affected by large matrix effect corrections (e.g., Cr- and Ti-rich oxides where FeLα is strongly absorbed), for which the self-absorption-induced shift of FeLα is different from that of common silicates and glasses.

INTRODUCTION

The redox state of Earth's mantle is a critical parameter to constrain models on the origin and the evolution of the Earth. Oxygen fugacity plays an important role in volatile speciation,

physical properties of mantle rocks, core-mantle interactions, and the atmospheric chemistry through time (Kadik and Lukanin 1985; Kasting et al. 1993). The redox state of the upper mantle is commonly estimated through values of oxygen fugacity calculated on the basis of Fe²⁺/Fe³⁺ equilibrium among mineral assemblages such as olivine-orthopyroxene-spinel (Ballhaus et al. 1990; O'Neill et al. 1993) or determined by

* E-mail: fialin@ccr.jussieu.fr

wet chemical analyses on minerals or glasses (Christie et al. 1986). For example, systematic relationships have been pointed out between upper mantle oxidation states and tectonic regimes (e.g., Wood et al. 1990; Canil et al. 1994). However, the effects of different processes on mantle redox conditions are still debated: are the large variations in the redox state linked to C-O-H fluids (Mattioli et al. 1989) or do they result only from magmatic processes, partial melting, and melt infiltration (Amundsen and Neumann 1992; McGuire et al. 1991)? Many of the controversies about this subject ultimately relate to the paucity and irrelevance of the available data. This lack of data may be the major justification for continuing to search for techniques of determining $\text{Fe}^{3+}/\Sigma\text{Fe}$.

Iron commonly occurs in two different oxidation states. The redox state of Fe is strongly dependent on the interaction with C-O-H fluids in natural magmas. These fluids play quite different structural roles (Waychunas et al. 1988; Cooney and Sharman 1990; Jackson et al. 1990) and have considerable influence on properties of silicate melts such as density or viscosity. The effect of the oxidation state of Fe and oxygen, the changes in $\text{Fe}^{3+}/\Sigma\text{Fe}$, and interactions of Fe and O in silicate melts have been widely debated (e.g., Dyar 1985; Mysen 1988). The determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ along with the sites occupied by Fe^{3+} and Fe^{2+} cations and their relationships with the silicate framework provide a basis from which the thermal history, and hence the melting processes by which a particular natural glass has formed, may be deduced.

Different methods are commonly used to measure $\text{Fe}^{3+}/\Sigma\text{Fe}$ in silicates and glasses and will be briefly reviewed in the next section. Extracting quantitative $\text{Fe}^{3+}/\Sigma\text{Fe}$ values from the $\text{Fe}L\alpha,\beta$ emission spectra measured with the EMP has been a long-term subject of study in geological applications (see Höfer et al. 1994 for a history of the related works over the past 35 years). Actually three ways have been investigated to process the $\text{Fe}L\alpha,\beta$ spectra: (1) measurement of the $L\alpha$ peak shifts; (2) measurement of the change in $L\beta/L\alpha$ intensity ratios; and (3) a hybrid of 1 and 2 (Höfer et al. 1994, 2000).

We present in this study a technique based on method (1) that is applicable to minerals and glasses for which the total Fe concentration (in wt%) has been previously established. The limitations of the method are discussed.

EXISTING METHODS FOR THE DETERMINATION OF $\text{Fe}^{3+}/\Sigma\text{Fe}$

Bulk methods

Several bulk methods have been developed to determine Fe^{3+} in silicate minerals. (1) Volumetric and colorimetric methods were proposed by Wilson (1960). Decomposition of the sample is carried out at room temperature by hydrofluoric acid containing V^{5+} to oxidize Fe^{2+} as it passes into solution. Between 50 and 200 mg of carefully hand-picked glass is required for this method. (2) Electrochemical cells (e.g., Sato 1970; Kadik 1997) also may be used for measuring oxygen fugacities, but reduction of the Fe^{3+} during experiments with C-bearing samples provides low f_{O_2} values (Virgo et al. 1988). (3) In Mössbauer spectroscopic analysis, $\text{Fe}^{3+}/\Sigma\text{Fe}$ can be determined directly from the relative areas of the Fe^{3+} and Fe^{2+} quadrupole

split doublets. A major advantage of the technique is that any uncertainty in the total Fe content of the sample does not affect the $\text{Fe}^{3+}/\Sigma\text{Fe}$, because the Mössbauer spectroscopy involves only deconvolution of the spectral data. In contrast, large uncertainties occur when $\text{Fe}^{3+}/\Sigma\text{Fe}$ is so low that the high-velocity component of the Fe^{3+} doublet is no longer discernible in the spectral data. This is usually the case for phases with less than 10% Fe^{3+} (i.e., $\text{Fe}^{3+}/\Sigma\text{Fe} < 0.1$). In addition, the spectra of amorphous solids are less well defined than those of their crystalline analogs (e.g., Mao et al. 1973; Eibschutz and Lines 1982), which introduces some uncertainties in the least-squares fitting used for the deconvolution procedure. (4) Millimetric X-ray beams, and related X-ray photoelectron spectroscopy or XPS, can be used by analyzing the Fe^{2+} and Fe^{3+} photopeaks emitted from the sample (Raeburn et al. 1997a, 1997b). Owing to the low escape depth of the photoelectrons (typically 5 nm) the method is very surface sensitive, which requires enhanced sample preparation to prevent surface contamination. Very low $\text{Fe}^{3+}/\Sigma\text{Fe}$ (down to 2%) can be measured by this method with uncertainties below $\pm 10\%$ relative. (5) Crystal field absorption spectroscopy with millimetric near-IR-visible-UV sources gives information on the oxidation state, coordination number, and geometry of the cation sites by processing the $d \rightarrow d$ transitions in the UV-visible region (200 nm) (Burns 1993). In theory, the intensity of the absorption bands allows the researcher to determine the concentration of the cation in its various oxidation states using the Beer-Lambert relationship (e.g., Bingham et al. 1999). For Fe, however, measurement of the Fe^{3+} band, of low intensity compared to Fe^{2+} , is rendered difficult by the presence of an intense absorption background due to intervalence charge transfer (IVCT) between Fe^{2+} and Fe^{3+} cations ($\text{Fe}^{2+} 3d \rightarrow \text{Fe}^{3+} 3d$ transitions, below for more comments on IVCT mechanisms).

The major criticism against bulk methods concerns the purity of the samples. Even carefully hand-picked glasses or minerals may contain traces of some other material that significantly changes the $\text{Fe}^{3+}/\Sigma\text{Fe}$ value.

Microbeam methods

To avoid contributions from undesirable phases, micro-beam techniques are particularly useful. Selection of surfaces from natural glasses or minerals that are free of any alteration, cracking, or secondary veins can be made by optical examination even at a scale of about 5 μm . Furthermore, these techniques are also useful for experimental materials, with dimensions ranging from few hundred micrometers to few millimeters, which cannot be processed by the common bulk methods cited above. Finally, it is important to emphasize that, unlike bulk methods, a quantity of about 1 μg can in theory be processed using microbeams. The Mössbauer method has been adapted to the study of samples with an area as small as 100 μm^2 with the development of the milliprobe (McCammon et al. 1991). The main disadvantage of the later method is the long time exposures required to balance the weak intensity of the beam.

The local determination of the oxidation states of Fe using both electron and X-ray spectroscopies has become more and more popular as a consequence of the development of modern micro-beam sources (electrons or X-rays). Active research on

synchrotron-based, high-resolution micro-XANES (X-ray near edge absorption structure) at FeK- and L-edges is in progress in connection with computer simulations to provide information on chemical bonding and oxidation states (Cressey et al. 1993; de Groot 1994; Brown et al. 1995; Westre et al. 1997; Delaney et al. 1998). This method promises to provide information on oxidation states and site occupancy of Fe in magmas where data for both remain controversial. Dramatic increase of the spatial resolution has been achieved by the development in the transmission electron microscope of ELNES (energy-loss near-edge structure spectroscopy), the equivalent of XANES for electrons, which allows the determination of Fe²⁺/ΣFe at the 10 nm scale by probing the FeL- and M-edges (van Aken et al. 1998, 1999; Garvie and Buseck 1998). For the EMP, Fe²⁺/ΣFe can be determined by Höfer's technique (cited above) using calibration curves constructed from precise measurements on reference materials. Using separate calibration curves for each mineral group, the precision and accuracy of Fe²⁺/ΣFe with this later method is 2% (absolute).

EXPERIMENTAL METHODS

Instrumentation

Measurements were carried out with a Cameca Camebax EMP, operating at 15 keV, using TAP monochromator crystals ($2d = 2.575$ nm). The FeL α peak maximum was located by using the regular automatic routine of the Cameca EMP software. The time required for a single peak search was 60 s, leading to an uncertainty of about ± 8 Bragg sin angle ($\sin\theta$) increments (1 increment = 1.10^{-3} $\sin\theta$) in the FeL α peak position for Fe concentrations ranging 5 to 30 wt% with a beam current of 40 nA. The pulse height analyzer was set to avoid the interference of FeL α with the high-energy ninth-order FeK α peak.

Sample description

The method for determining Fe²⁺/ΣFe is based on two calibration stages, for which two specific groups of both hydrous and anhydrous minerals have been selected, together with natural and synthetic glasses. For the first calibration stage, the following anhydrous minerals containing either Fe²⁺ or Fe³⁺ were selected: (1) *clinopyroxenes* (diopside and hedenbergite, with 3 and 16 wt% Fe²⁺ respectively, and acmite with 19 wt% Fe³⁺); (2) *orthopyroxene* with 9 wt% Fe²⁺; (3) *olivines* with 3–17 wt% Fe²⁺; (4) *garnets* (andradite with 22 wt% Fe³⁺ and almandine with 17 wt% Fe²⁺); (5) *K-feldspar* with 4 wt% Fe³⁺; (6) *epidote* with 7 wt% Fe²⁺; and (7) *staurolite* with 9.9 wt% Fe²⁺.

For the second calibration stage, samples with varying Fe²⁺/ΣFe have been selected. Mineral species were (1) *clinopyroxenes* (six minerals) with 5–23 wt% Fe and 15–96% Fe²⁺/ΣFe; (2) *garnets* (four minerals) with 5–20 wt% Fe and 47–90% Fe²⁺/ΣFe; (3) *Al-rich spinels* (seven minerals) with 9–17 wt% Fe and 14–75% Fe²⁺/ΣFe; (4) *amphiboles* (two minerals) with 7–10 wt% Fe and 95–98% Fe²⁺/ΣFe; (5) *micas* (four minerals) with 8–18 wt% Fe and 15–33 Fe²⁺/ΣFe. The following 25 glass samples also were studied: (1) *tholeiitic* (16 natural samples) with 7–10 wt% Fe and 10–17% Fe²⁺/ΣFe; (2) *basaltic lava* (six samples obtained by fusion of powdered natu-

ral glasses at 1270–1300 °C under controlled air fluxes to obtain the required Fe²⁺/ΣFe) with 6–8 wt% Fe and 30–85% Fe²⁺/ΣFe; and (3) *andesitic* (three synthetic samples, same treatment as for the basaltic glasses) with 5–16 wt% Fe and 50–64% Fe²⁺/ΣFe. The essential data on mineral and glass compositions used in this study are presented in Table 1. Values of Fe²⁺/ΣFe were either calculated by common stoichiometry and charge-balance relationships deduced from EMP analyses of anhydrous minerals, or measured by wet chemistry and/or Mössbauer spectroscopy for glasses (Humler et al. 1998; Neuville et al., unpublished data, 1999) and hydrous silicates (wet chemistry on separated minerals).

SELF-ABSORPTION OF LOW ENERGY L α PEAKS

The L-series peaks emitted from the first row transition metals are the result of radiative electronic transitions between the partially filled 3d orbitals to the 2p (or L_{2,3}) core levels. The energies of these peaks are below 1 keV. Several papers have described the L-series of light transition metals, as well as those of Cu and Zn (Parratt 1959; Holliday 1968; Bonnelle 1987), and point out the large contribution of self-absorption (i.e., absorption by its own atoms or ions of X-ray photons emitted from a chemical species) in misinterpretation of experimental spectra. Indeed, self-absorption is responsible for asymmetries on the high-energy side of the L-peaks, leading to peak position shifts and changes in the L β /L α ratio (O'Nions and Smith 1971; Rémond et al. 1996). These spectral distortions are caused by the large contrasts in absorption coefficients on either side of the metal L_{2,3} edges that are in close proximity to the L α peak maxima. The full widths at half maximum (FWHM) of low-energy L peaks is the convolution of the natural widths of both 3d and 2p levels. The energy distributions of the 2p levels are described by Lorentzian curves with widths inversely proportional to the lifetime of the 2p-core holes. The 2p level width is ~1.5 eV in Fe (Bonnelle 1966). In addition, the final state hole causes the 3d band to broaden. Similar peak broadenings related to the lifetime of the ionized state affect the 2p absorption spectra (de Groot et al. 1990). Self-absorption occurs when lifetime broadenings are large enough to initiate overlap between both emission and absorption bands. Due to the later intrinsic loss of resolving power of the method, photons are generated with the minimal energy required for transitions from the 2p core level to continuum states (empty states just above the Fermi level, E_f, for low energy peaks). Empty states at E_f for transition metals are composed of admixtures of 3d and 4sp states. In applying dipole selection rules, transitions of core electrons (as 2p electrons) to localized empty states (e.g., 3d) dominate over delocalized conduction states (e.g., 4sp). Both types of transitions may dramatically change the shape of the L_{2,3}-edge with strong effects on the self-absorption. A classical example is given by the comparison of the CuL_{2,3} absorption spectra of Cu₂O and CuO (e.g., Bonnelle 1966). The L_{2,3} discontinuity of the former is arctangent shaped, which is characteristic of 2p → 4s transitions (low self-absorption of CuL α), whereas that of the later consists of a white-line (i.e., is peak shaped) as a consequence of highly probable transitions to the 3d-hole localized on the e_g orbital (high self-absorption of CuL α). Therefore, the self-absorption intensity of soft L α peaks